

2-hydroxypropyl (meth)acrylate, glycidol di(meth)acrylate, caprolactone denatured 2-hydroxyethyl (meth)acrylate, pentaerythritol tri(meth)acrylate, and glycerol diacrylate. These may be used alone or in the combination of two or more. The word "(meth)acrylate" means any one of acrylate and methacrylate in the present invention.

The urethane oligomer (A) of the present invention can be produced by a process as described below for example.

The polyol compound (a) is reacted with the polybasic acid anhydride (b-1) to produce the terminal alcohol compound (hereinafter called a carboxyl group-containing terminal alcohol compound) having at least two carboxyl groups, which is then reacted with the polyisocyanate compound (c) to get a carboxyl group-containing terminal isocyanate urethane prepolymer. The urethane prepolymer thus obtained is reacted with the ethylenically unsaturated group-containing hydroxy compound (d) to obtain the urethane oligomer (A) of the present invention.

The polyol compound (a) is preferably reacted with the polybasic acid anhydride (b-1) in such a rate that the amount (equivalent) of the acid anhydride group of the latter (b-1) is 0.5-0.99 equivalent per 1 equivalent of hydroxy group of the former (a). This esterification can be carried out by a publicly known method, preferably at a reaction temperature of 60-150°C

T05060323811600

TOSOGO-SZB11060

and for a reaction time of 1-10 hours. An amine compound such as triethylamine may be added at 0.1-5% for the reaction catalyst.

The reaction for obtaining the carboxyl group-containing terminal isocyanate urethane prepolymer is preferably carried out in such a rate that the isocyanate group of the polyisocyanate compound is 1.1-2.1 equivalent per 1 equivalent of hydroxy group of the carboxyl group-containing terminal alcohol compound as obtained above. The reaction for prepolymerizing is generally carried out at a room temperature -100°C, preferably at 50-90°C.

To obtain the urethane oligomer (A) of the present invention, the above terminal isocyanate urethane prepolymer is preferably reacted with the ethylenically unsaturated group-containing hydroxy compound (d) in such a rate that the hydroxy group of the hydroxy compound (d) (preferably, hydroxyalkyl(meth)acrylate) is 0.9-1.5 equivalent per 1 equivalent of isocyanate group of the prepolymer. The especially preferable rate is 1.0-1.1.

The last reaction step for obtaining the urethane oligomer (A) is generally carried out at a room temperature-100°C, preferably at 50-90°C. It is desirable that a polymerization inhibitor such as hydroquinone, hydroquinone monomethyl ether, p-methoxyphenol and p-benzoquinone is generally added at 50-2,000ppm to prevent gelatinization by

radical polymerization. A catalyst such as triethylamine, dibutyl tin laurate and dibutyl tin diacetate, preferably dibutyl tin laurate, may be added in the reaction system, though the hydroxy group can be reacted with the isocyanate group even in the absence of a catalyst.

The reactive diluent (C-1) and/or the non-reactive diluent (C-2) as described below may be used for a diluent (C) while the reaction lasts or after it ends.

The non-reactive diluent (C-2) includes an aromatic hydrocarbon such as toluene and xylene; an ester such as ethyl acetate and butyl acetate; an ether such as 1,4-dioxane and tetrahydrofuran; a ketone such as methyl ethyl ketone and methyl isobutyl ketone; a glycol derivative such as butyl cellosolve acetate, carbitol acetate, diethylene glycol dimethyl ether and propylene glycol monomethyl ether acetate; an alicyclic hydrocarbon such as cyclohexanone and cyclohexanol; and a petroleum solvent such as petroleum ether and petroleum naphtha. These may be used alone or in the combination of two or more.

The carboxyl group of the urethane oligomer (A) can be neutralized with a basic compound to change into the salt of the urethane oligomer (A')(The salt is called "a water-soluble urethane oligomer (A')" hereinafter).

The basic compound to use for preparing the salt of the